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Effect of Collisional Lifetime in Optoacoustic Detection of Pollutant Gases

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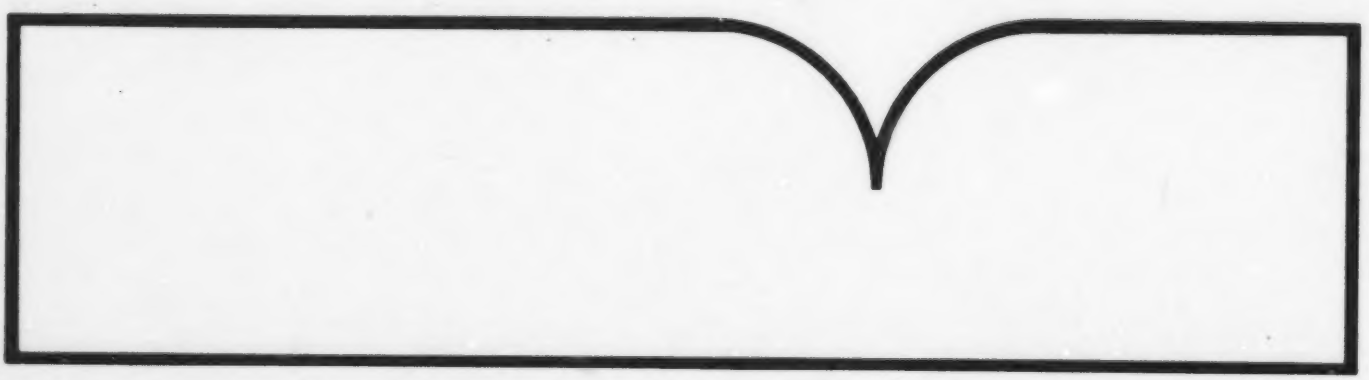

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EFFECT OF COLLISIONAL LIFETIME IN OPTOACOUSTIC DETECTION OF POLLUTANT GASES

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16. ABSTRACT

The optoacoustic technique shows promise for pollution monitoring due to its small size and high sensitivity. This technique is fundamentally different from most spectroscopy in that absorbed energy is measured indirectly as a pressure change in the surrounding gas. Not all the absorbed energy is detected as a pressure change, the actual value depending on the collisional and thermal relaxation times. This research shows that relaxation effects in carbon dioxide begin to reduce the optoacoustic signal below 100 Torr. At 50 Torr the optoacoustic signal contains only half the absorbed energy. Collisional and thermal relaxation times of 7.5 μ sec and 0.1 sec are shown to correctly predict the decrease in the optoacoustic signal.

A new calibration technique employing a piezoelectric crystal was developed for this research. The piezoelectric calibration was necessary because the microphone sensitivity varied by a factor of 3 as a function of total gas pressure. This technique is generally applicable in accounting for changes in microphone sensitivity.

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ABSTRACT

The optoacoustic technique shows promise for pollution monitoring due to its small size and high sensitivity. This technique is fundamentally different from most spectroscopy in that absorbed energy is measured indirectly as a pressure change in the surrounding gas. Not all the absorbed energy is detected as a pressure change, the actual value depending on the collisional and thermal relaxation times. This research shows that relaxation effects in carbon dioxide begin to reduce the optoacoustic signal below 100 Torr. At 10 Torr and 200 hz the optoacoustic signal is only half that at atmospheric pressure. Collisional and thermal relaxation times of 7.5 μ sec and 0.1 sec are shown to correctly predict the decrease in the optoacoustic signal.

A new calibration technique employing a piezoelectric crystal was developed for this research. The piezoelectric calibration was necessary because the microphone sensitivity varied by a factor of 3 as a function of total gas pressure.

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SECTION 1

INTRODUCTION

In 1881, Alexander Graham Bell[1] observed that audible sound can be produced by illuminating a gas with intensity modulated infrared radiation through a transparent, constant volume container Bell realized the possibility of using this effect for studies of the spectral absorption of gases. He proposed the name "spectrophone" for the instrument to do this. The phenomenon is now called the opto-acoustic effect, or simply optoacoustic effect. Little work was accomplished in the few short years following 1881, mainly due to the lack of a sensitive pressure measuring device (e.g. condenser microphone). The optoacoustic effect was forgotten until 1938, when Veingerov[2,3,4] renewed interest by executing a series of quantitative and qualitative experiments on gas mixtures. Over the years, development has increased and a number of optoacoustic gas analyzers were constructed[2,5].

The use of the spectrophone for the measurement of vibrational-translational relaxation times was first suggested by Gorelik[6] and later by Cottrell[7]. Extensive theoretical work has been completed in the area of the spectrophone[8,9], and the measurement of relaxation times[10,11].

The present experiment consisted of three segments. The first required the building of a CO_2 gas laser and spectrophone with the required electronics and gas handling devices. The second segment required calibration of the equipment and the design of the experimental procedure. The third segment dealt with obtaining and analyzing the data. The gases analyzed were carbon dioxide (CO_2) and nitrous oxide (N_2O). The relaxation times obtained are in agreement with ultrasonic methods.

SECTION 2

THEORY OF THE OPTOACOUSTIC EFFECT

2.1 Absorption of infrared radiation

When a molecule absorbs infrared radiation, the energy taken up appears directly as quanta of vibrational energy. An absorbing molecule may lose this energy by one of three processes:

1. Spontaneous emission of radiation
2. Induced emission
3. Transfer of energy during a collision

For low intensity incident radiation, the probability for induced emission is much less than that of spontaneous emission, and the energy loss by induced emission is negligible. Therefore, the radiative process will refer to the energy loss by spontaneous emission only.

The transfer of energy during a collision is the energy loss from the vibrational degrees of freedom of the molecule. If the infrared radiation absorbed by the vibrational degrees of freedom were immediately converted to translational energy, the temperature should be a maximum when the beam is cut off. Since a large number of collisions are required to equilibrate the vibrational degrees of freedom, there is a finite time delay between the light intensity pulse and the temperature increase. This time delay and its relation to the time delays in collisional energy transfer will be discussed later. It is the fact that the absorbing gas temperature increases that is of importance for the optoacoustic effect.

Therefore, if the absorbing gas is illuminated by infrared radiation which is periodically interrupted or intensity modulated, the gas will heat and cool and a periodic change in pressure will be observed in a constant volume system. If the frequency of modulation is in the sonic range, these changes in pressure will give rise to sound emission.

2.2 Energy transfer in the optoacoustic effect

The optoacoustic cell consisted of a volume of gas whose linear dimensions were small compared with the length of the sound wave which corresponds to the frequency of modulation of

the infrared radiation. At a frequency of 200 hz the wavelength of a sound wave is about 150 cm, and at 1000 hz it becomes about 30 cm, so this condition is easily obtained. It can be shown that the acoustic pressure should be proportional to the incident intensity, and the absorption coefficient for constant composition[10]. Rosengren[12] considers three major relaxation processes acting to reduce the acoustic pressure signal. First some molecules lose their energy through radiative transition. This energy does not appear in the optoacoustic signal. The fraction of molecules losing energy by collision is $t_r/(t_r + t_c)$, where t_c is the collisional relaxation time and t_r is the radiative relaxation time.

The second process is due to collisions with the cell wall. The higher the chopping frequency, the less likely that a molecule will diffuse to the cell wall and the smaller the contribution of heat loss to the walls of the cell. This process reduces the optoacoustic signal by the factor $wt_t/(1 + w^2 t_t^2)^{\frac{1}{2}}$, where t_t is the thermal relaxation time of the cell.

The third relaxation process takes into account the upper state lifetime. If the chopping period is much shorter than the time needed for the upper state to depopulate, a population build-up will occur and effectively reduce the signal amplitude. This expression is given by: $\{1 + (w(1/t_c + 1/t_r)^{-1})^2\}^{-\frac{1}{2}}$.

The expression for the acoustic pressure accounting for relaxation effects can now be written as:

$$P(t) \propto \frac{N}{V}\sigma \frac{t_t}{(1 + t_c/t_r)(1 + (wt_t)^2)^{\frac{1}{2}}(1 + (w(t_c^{-1} + t_r^{-1})^{-1})^2)^{\frac{1}{2}}},$$

where N is the number of molecules in the cell volume V. The absorption cross section for the actual radiation is σ. This equation was used to fit the experimental data from the amplitude measurements.

2.3 Effects of Line Profile

Any atomic or molecular transition has an inherent finite spread of energy or frequency. There are three processes which contribute to the finite width of the spectral line in varying degrees: natural broadening, Doppler broadening, and collisional broadening. These effects determine the frequency dependence of the absorption coefficient of the gas. Since collisional broadening predominates above a few Torr only its effect will be discussed here. The laser line stimulating the vibrational mode in the molecule will be considered as an ideal monochromatic "line".

The presence of other atoms results in collisions which have the effect of truncating the wave trains of the molecules undergoing transition. The frequency dependence of the absorption coefficient can be shown to be

$$\sigma(f) = C \frac{\frac{1}{2}\pi t_c}{(f-f_o)^2 + (\frac{1}{2}\pi t_c)^2}$$

where f_o is the line center frequency, t_c is the mean time between collisions and C is constant depending on the line strength. If the incoming radiation is at line center this equation reduces to

$$\sigma = \frac{2C}{\pi t_c}$$

Therefore the absorption coefficient becomes inversely proportional to the mean collision time. This condition is shown in figure (2.1) where the laser line is depicted as the monochromatic line at frequency f_o. The absorption coefficient becomes inversely proportional to the pressure for on line center absorption. This is due to the fact that t_c is inversely proportional to the pressure.

Off line center the absorption coefficient retains its Lorentzian shape as a function of frequency. Now the absorption coefficient is a function of both frequency and pressure. If the incident radiation is within the half width of the absorption profile, then the signal increases with decreasing pressure.

For values around the half width, the signal may increase and decrease as a function of pressure. For incident radiation in the wings, the signal is directly proportional to the pressure as shown in figure 2.1.

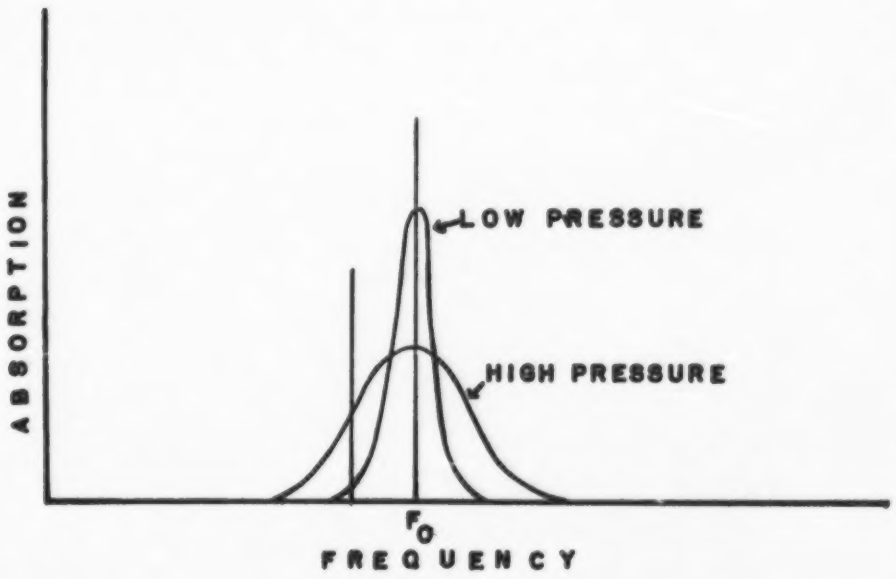

Figure 2.1: Absorption line profile at high and low pressure.

SECTION 3

APPARATUS AND PROCEDURE

The experimental set-up is shown in figure 3.1. The apparatus consists of a CO_2 laser, light chopper, two sample cells and lock-in amplifiers. The power cell is a simple brass tube with microphones epoxied to the cell wall. It is used only as a beam reference in the experiment. The spectrophone is more elaborate and is shown in figure 3.2. It can be operated at various total pressures and has a piezoelectric crystal incorporated in the wall for calibration.

3.1 Optoacoustic Cell

The optoacoustic cell is shown in figure 3.2. The cell was cylindrical in shape, being 8.3 cm in length with a diameter of 2.0 cm. The microphone cavity and the active cell cavity were connected during actual measurement but closed off during a pressure change. The windows were NaCℓ disks 2.3 cm in diameter.

Pressure changes in the cell were detected by three electret condenser type microphones (Knowles Electronics, Mdl-BT-1759) which gave good spacial averaging and a flat frequency response over the audio range. The microphones employed an integrated FET for signal amplification.

It was noticed that the microphone sensitivity varied by a factor of 3 over a pressure range of 10 to 760 Torr. This sensitivity variation is due to the decreased pressure in the air pockets behind the electret foil which provide the restoring force for microphone operation. A new calibration technique was developed in order to calibrate for this change in sensitivity.

The optoacoustic cell was calibrated by attaching a piezoelectric crystal to the cell wall. The crystal changes its length in response to an applied electric field allowing precise volume, and hence pressure changes in the cell. The crystal was biased at about 200 volts and modulated by an AC generator at a peak voltage of about 40 volts. The change in sensitivity as a function of pressure is shown in figure 3.3. The optoacoustic signal obtained during actual measurements was divided by the sensitivity to give the corrected signal.

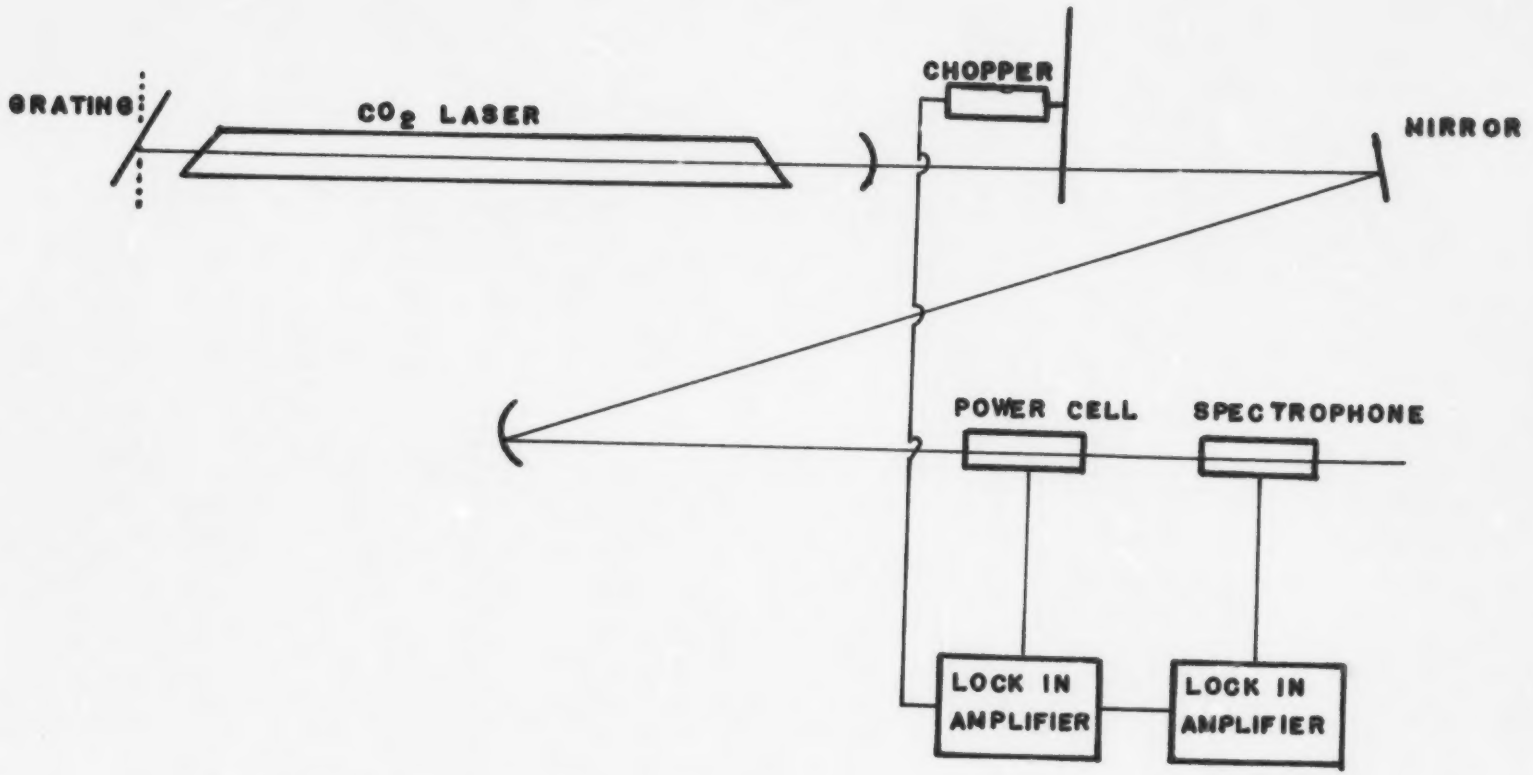

Figure 3.1: Experimental set-up.

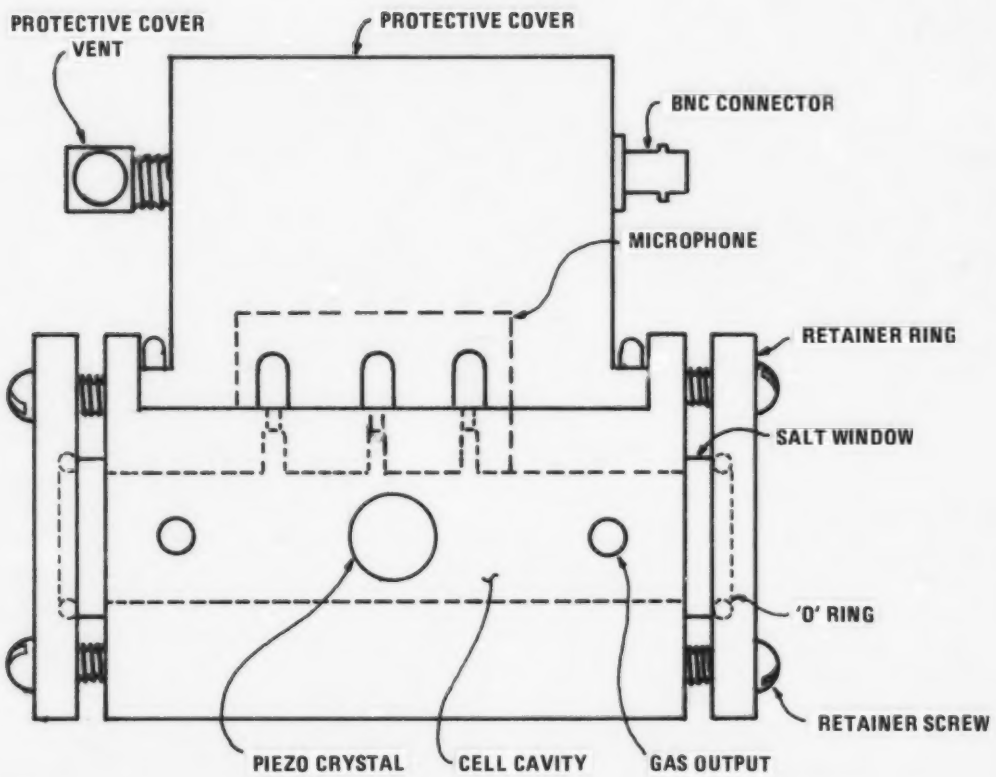

Figure 3.2. Spectrophone

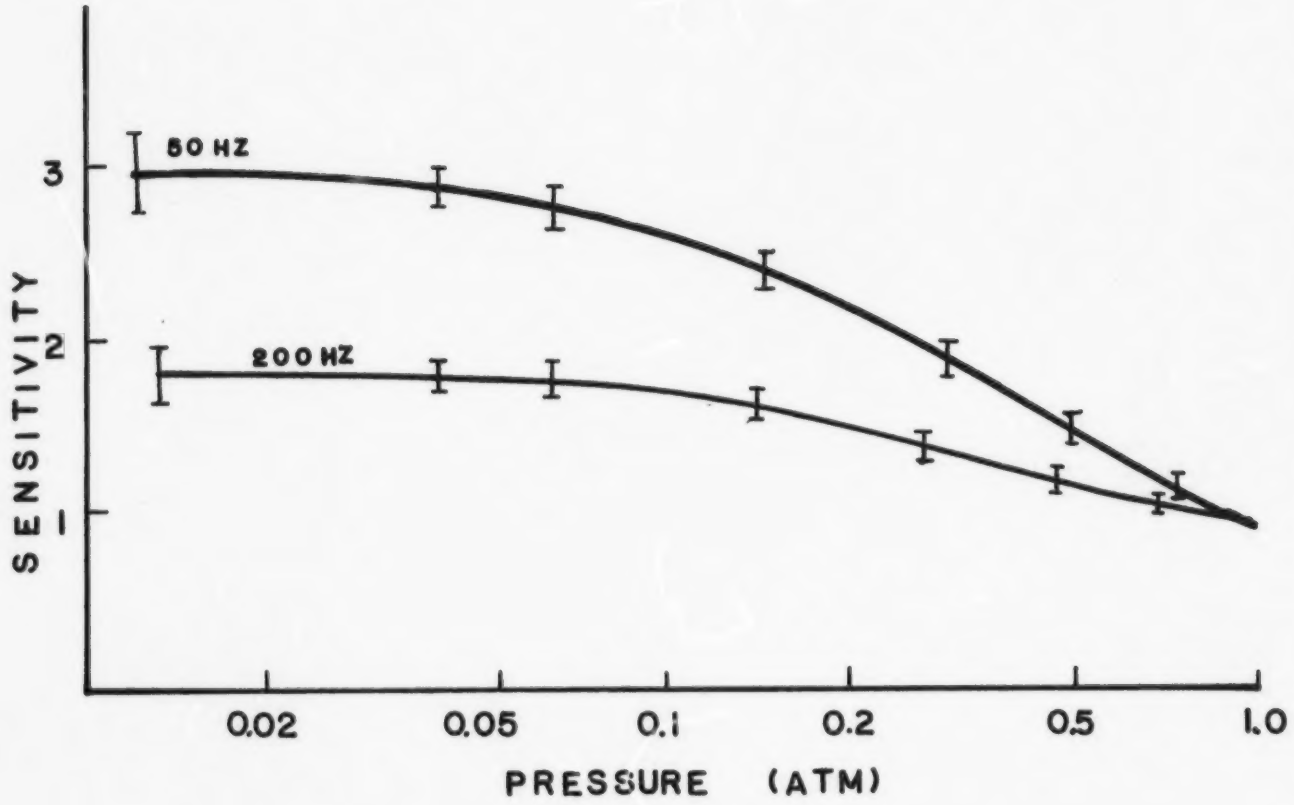

Figure 3.3: Microphone sensitivity vs total gas pressure.

3.2 Procedure

Prior to taking data, the system was pumped down to < 1 micron as measured by a thermocouple vacuum gauge. The lock-in amplifier was calibrated for the specific chopping frequency and the appropriate wavelength of the CO_2 laser was selected by altering the angle of the grating. The signal measuring devices were nulled and the microphone battery levels checked.

The following procedure was executed at each gas pressure. The gas pressures were chosen for a logarithmic scale.

Gas

1. The three valves were opened to the cell.
2. The gas under study was selected and allowed to enter the system to a given pressure value.
3. The system was allowed to equilibrate and then closed off.
4. A pressure reading was taken.

Microphone response

1. The laser beam was blocked.
2. The piezo electric crystal was energized at the specific chopping frequency.
3. The phase was adjusted to give maximum output on the lock-in amplifier.
4. The output from the lock-in amplifier was recorded.
5. The phase measurement was recorded.

Signal

1. The piezo crystal was disabled.
2. The laser beam was allowed to pass through the cells.
3. The lock-in amplifier was adjusted for maximum output.
4. The dual pen strip chart recorder was activated and the signal level and power level were recorded concurrently.
5. The phase was recorded.
6. The data was averaged and recorded.

After the data was recorded, the sensitivity of the microphones was calculated and normalized to unity at one atmosphere. The signal was divided by the power level and divided by the normalized sensitivity to give the corrected signal. The corrected signal was normalized and used as input to a computer program to fit the relaxation times.

SECTION 4

RESULTS

4.1 Carbon Dioxide

The optoacoustic signal, corrected for microphone effects, is shown as a function of pressure for CO_2 in figure 4.1. The decrease in signal at low pressure is due to relaxation effects as discussed previously. The relaxation times were determined from this data by use of a standard chi-squared minimization program. Chi-squared is given by the formula

$$X^2 = \frac{1}{n} \sum_{i=1}^{n} \frac{(YT(i) - YD(i))^2}{(STD(YD(i))^2}$$

Where YT denotes the calculated point, and YD the data point for n data points. STD is the standard deviation for each experimental point. The thermal, collisional and radiative lifetimes were varied in Rosengren's equations until a best fit was obtained. Plots of the chi-squared value as a function of the relaxation time are shown in figure 4.2. If the chi-squared value does not change appreciably over large changes in the relaxation time (50%), then the accuracy of the relaxation time should be questioned. Figure 4.2 shows that the radiative relaxation time cannot be determined accurately by fitting the optoacoustic amplitude.

Since the thermal relaxation time is dependent on cell geometry, an alternative method for its determination was devised. A Q-switched laser pulse was passed through the optoacoustic cell and the slow decrease in pressure as the cell returned to equilibrium was used to calculate the thermal relaxation time. A value of 0.10 ± 0.01 sec was obtained in agreement with the least squares fitting program (see Appendix A).

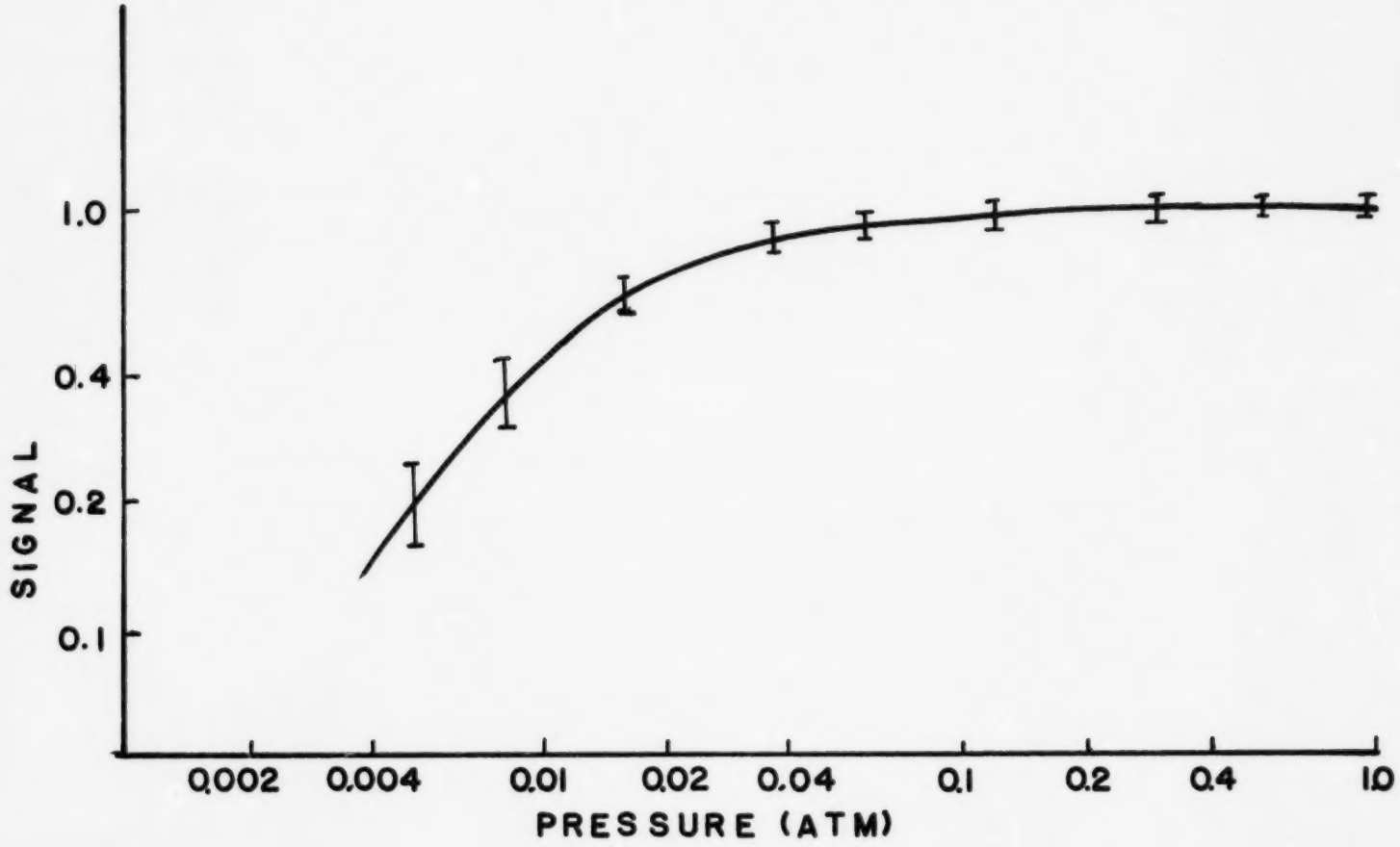

Figure 4.1: Carbon dioxide optoacoustic signal as a function of pressure. (chopping frequency = 200 hz)

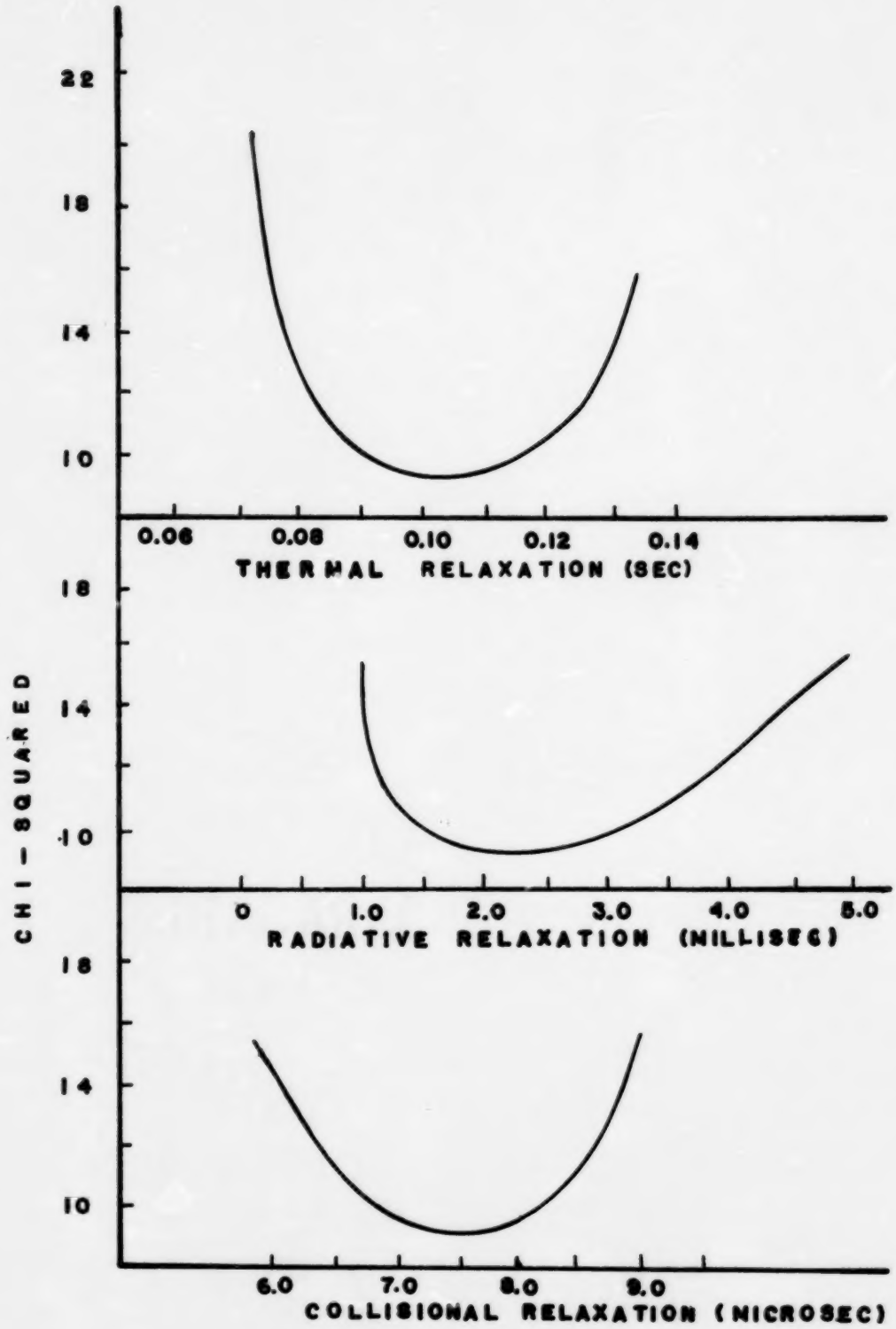

Figure 4.2: Chi-squared as a function of the three fitting parameters.

The result of 7.5 μ sec for the collisional relaxation time is in good agreement with other spectrophone and ultrasonic measurements of other authors shown in 4.1.

Table 4.1: Published Collisional Relaxation Times

Experimenters	Method	Results
Yardley & Moore[14]	Spectrophone	11.0 μ sec
Houghton[15]	Spectrophone	12.0 μ sec
Read[11]	Ultrasonic	9.0 μ sec
Cottrell[16]	Spectrophone	7.5 μ sec

4.2 Nitrous Oxide

Several data sets were obtained for nitrous oxide at the P(16) and P(24) laser lines in the 10 micron band. The data shown in figures 4.3 and 4.4 are plots of the absorption per molecure vs pressure. Figure 4.3 clearly shows the increase in absorption when the laser line is within the half width of the absorption line followed by a decrease in absorption as the laser line moves outside the half width at low pressure. Figure 4.4 shows the absorption for a laser line that is always outside the absorption half width. Relaxation times were not determined for the N_2O molecule because the absorption line half widths and the frequency separation between laser and absorption line center added two more parameters to the fitting routine.

4.3 Discussion

The results of optoacoustic measurements are seen to be in agreement with other methods. Collisional, radiative, and thermal relaxation times must be taken into account when reporting optoacoustic spectra at low pressure. In addition absorption line shape and position can greatly effect the absorption coefficient by increasing or decreasing the absorption with pressure.

Electret microphones have been shown to vary their sensitivity by a factor of three but this problem can be overcome by suitable calibration. The piezoelectric calibration is simple and straight forward and provides the experimenter with a technique that not only checks for variations in a particular data set but also checks for long term system variability.

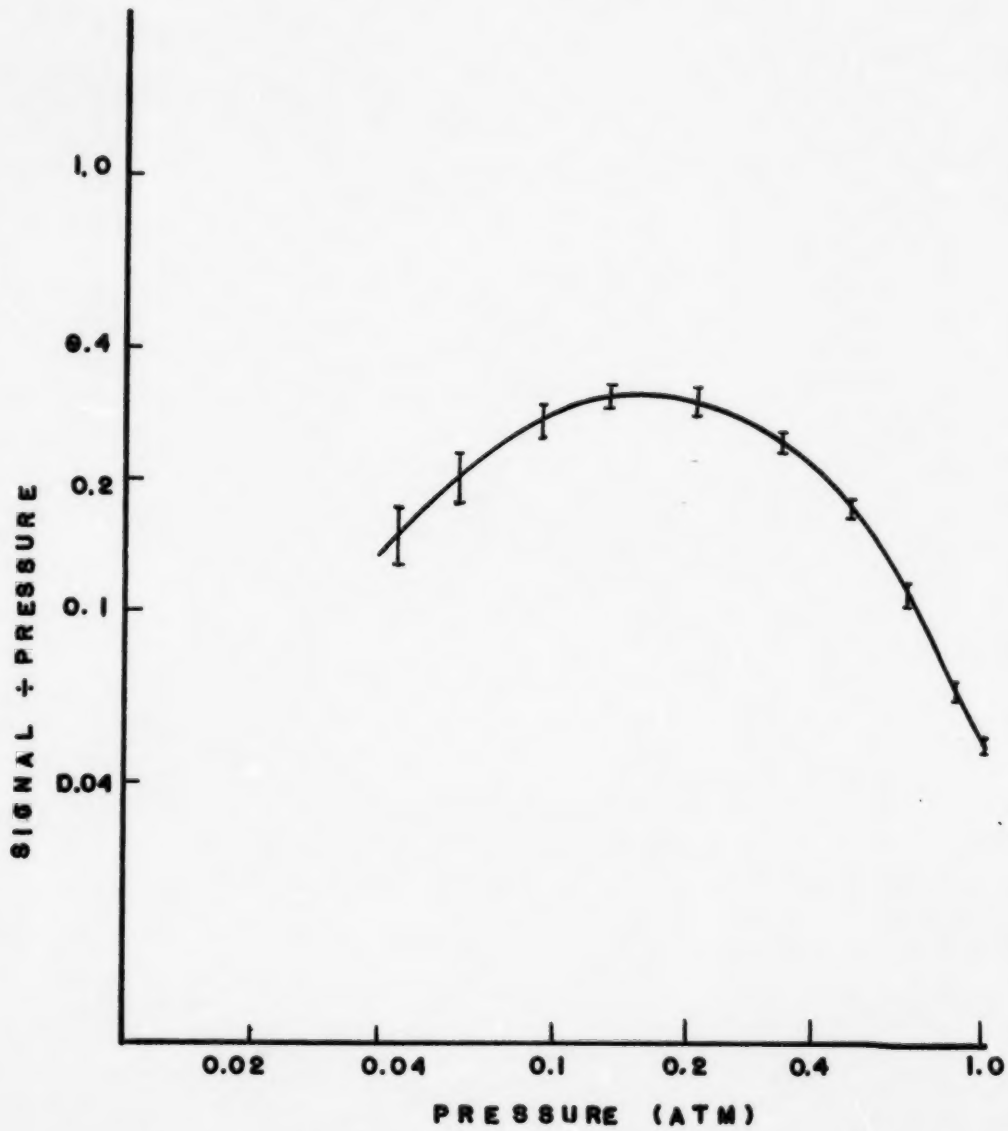

Figure 4.3: The absorption per molecule in N_2O as a function of pressure using CO_2 P(24) laser line for excitation.

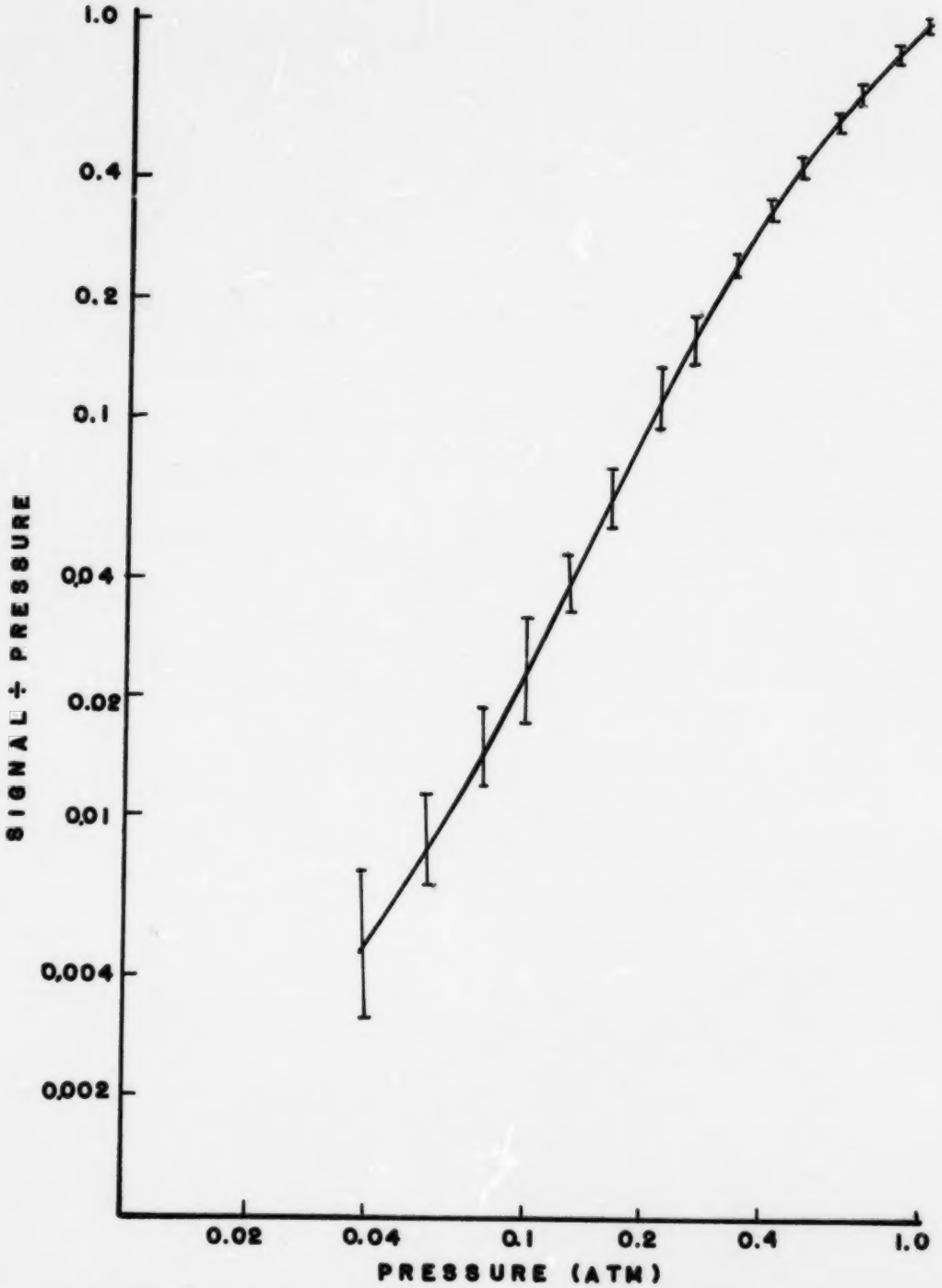

Figure 4.4: The absorption per molecule in N_2O as a function of pressure using CO_2 P(16) laser line for excitation.

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APPENDIX A

Paper Presented at Optical Society of America Topical Meeting on Photoacoustic Spectroscopy. Ames, Iowa 1979.

WB6P. A CALIBRATION TECHNIQUE FOR PHOTOACOUSTIC CELLS, W. Christian, Allegheny College, Meadville, Pennsylvania 16335.

A peizoelectric crystal was used to calibrate a photoacoustic cell in order to measure the CO_2 P(20) absorption at line center and the N_2O R(1) absorption off line center. A least square fitting of the CO_2 data to Rosengren's equation was used to find the radiative, thermal, and collisional relaxation times of the gas.

This research was supported in part by Environmental Protection Agency grant #R-806439-01 and the Sigma XI Society.

A Calibration Technique for Photo-Acoustic Cells.
W. Christian, Allegheny College, Box 36, Meadville, PA 16335.

A piezoelectric crystal was incorporated into the wall of a 10 cm long photo-acoustic (PA) cell. The crystal was modulated at 200 hz and the resulting pressure fluctuations were detected by Knowles Electronics Mdl. BT 1759 electret microphones attached to the cell wall. The resulting signal was detected with a lock-in amplifier. The PA detection was filled with CO_2 and the sensitivity of the microphone as a function of absolute pressure was obtained by plotting the microphone signal ÷ pressure vs pressure. Fig. 1 shows an increase in microphone sensitivity at low pressure due to the increased compressibility of the air in the pockets behind the electret foil.

A chopped CO_2 laser beam was then passed through the PA cell. The signal was measured as a function of absolute pressure and corrected for the variation in sensitivity with pressure. Fig. 2 shows that the

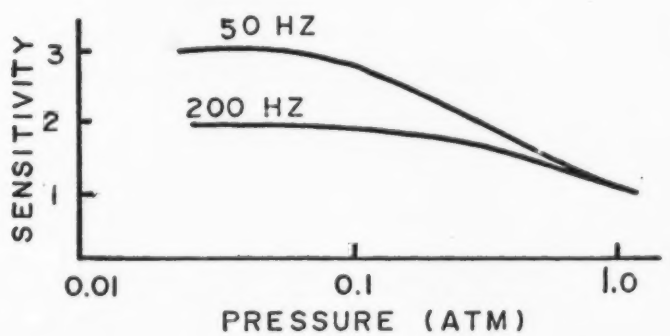

Fig. 1. Microphone sensitivity as a function of absolute pressure.

corrected signal is constant at high pressures but begins to decrease at low pressure. Since CO_2 is collision broadened at high pressures, reducing the pressure will decrease the number of absorbing molecules but increase the absorption per molecule. These effects should produce a constant absorption as the pressure is decreased. The decrease in PA signal that is observed is due to relaxation effects as predicted by Rosengren (1).

The thermal diffusion time of the PA cell was measured by passing a Q switched laser pulse through the cell. The resulting microphone signal was displayed on an oscilloscope and is shown in Fig. 3. Fig. 3 represents the time derivative of the pressure in the cell since electret microphones respond to changes in pressure. The rapid transfer of vibrational to translational energy is not resolved by the microphone but the subsequent pressure decrease due to thermal diffusion to the wall is clearly shown. The thermal diffusion time was measured to be 0.11 sec. at 760 Torr. Rosengren's analysis predicted the PA signal to within 3% when the thermal relaxation of the cell was set equal to 0.11 sec. and the collisional relaxation time was set equal to 9 μ sec. at atmospheric pressure.

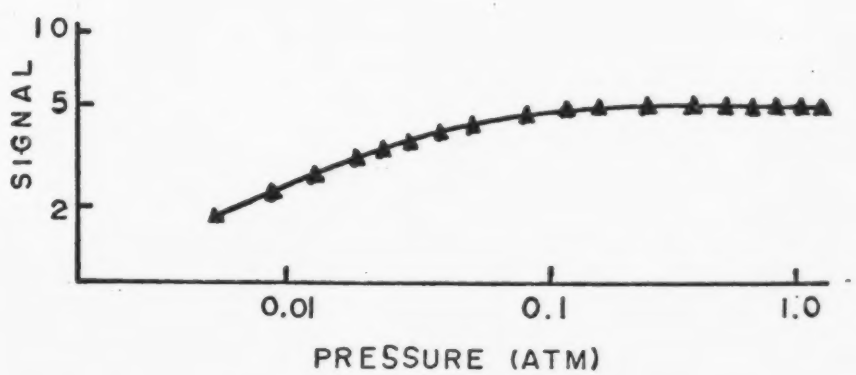

Fig. 2. The corrected photoacoustic signal for the CO_2 P(20) transition at line center as a function of pressure.

In order to investigate the effect of line shape on PA signals the cell was filled with N_2O and the PA signal again measured as a function of pressure. The PA signal was corrected for sensitivity variation in the microphone and relaxation effects. This corrected value was then divided by the absolute pressure to obtain the absorption per molecule shown in Fig. 4. The absorption increases initially because the P(24) CO_2 laser line is close to line center of the R(1) N_2O transition in the 10.6 micron band. As the pressure is decreased, however, the laser line falls outside the halfwidth of the N_2O line and the absorption decreases. The laser line is at the collisionally broadened halfwidth when the absorption is a maxima.

The piezoelectric calibration technique has been shown to be useful technique for the calibration of

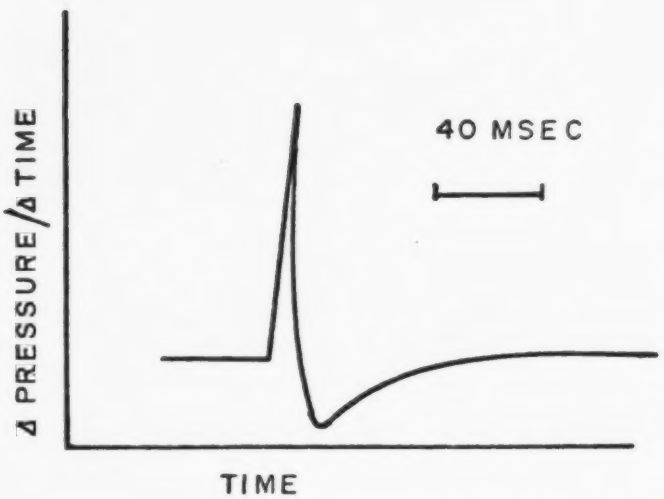

Fig. 3. The rate of change of pressure in a PA cell following the passage of a Q switched laser pulse. The cell pressure was 150 Torr.

PA cells. Once a cell has been calibrated it can be used to measure line shapes, self broadening, and foreign gas broadening coefficients of absorbing gases if the absorption lies sufficiently close to the pump laser line.

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(1) L. G. Rosengren, Appl. Opt., 14, 1960 (1975).

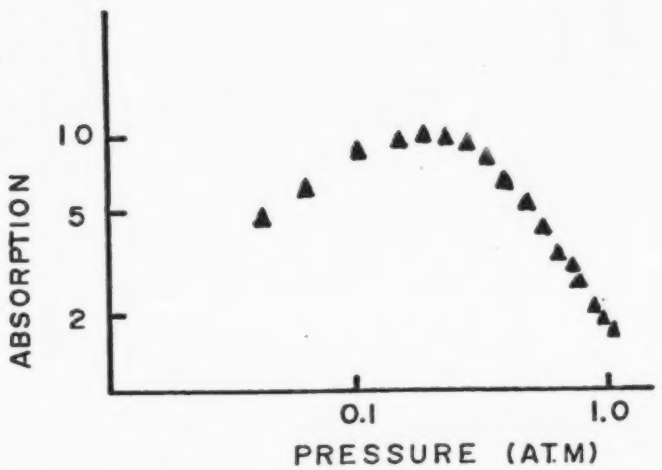

Fig. 4. The absorption per molecule of the R(1) 10.6 μ band transition in N_2O as a function of pressure. The incident radiation is from the CO_2 P(24) laser transition.